

Improvement of the thermal stability of hydrous zirconia by post-synthesis treatment with NaOH and NH₄OH solutions

G. Aguila, S. Guerrero, F. Gracia, P. Araya*

*Centro para la Investigación Interdisciplinaria Avanzada en Ciencias de los Materiales,
Departamento de Ingeniería Química, Universidad de Chile, Casilla 2777, Santiago, Chile*

Abstract

The structural stability of a commercial hydrous zirconia and a hydrous zirconia synthesized in our laboratory by the sol-gel method has been improved by a post-synthesis reflux treatment with aqueous NH₄OH and NaOH solutions (100 °C for 9 h). Direct calcination of both materials at 700 °C for 3 h, rendered zirconium oxides with a mixture of monoclinic and tetragonal structures and specific areas of 36 and 27 m²/g, respectively. In contrast, if the materials were refluxed before calcination with NaOH or NH₄OH solutions, zirconium oxides with tetragonal structure and specific areas between 90 and 200 m²/g were obtained after calcination at 700 °C. In the treatments with NaOH solution, addition of Si coming from dissolution of the flask glass walls or from an external Si source in a plastic flask is responsible for the stability of the final zirconium oxides. Nevertheless, the porous structure of these materials is determined by the treatment conditions in basic solution, thus allowing to control the physical properties of the final oxide. Short treatment times are sufficient to stabilize the hydrous zirconia. On the contrary, if the reflux is made with a NH₄OH solution, the stabilization mechanism appears to be different since there is no evidence of Si addition in the oxides. In this case, the pore size distribution strongly depends on the reflux time, and the highest specific area is obtained for the largest treatment time (9 h).

Keywords: Zirconium oxide; High surface area; NaOH treatment; NH₄OH treatment

1. Introduction

Zirconium oxide has been shown to be an excellent support to prepare catalysts for different uses. Particularly, Pd supported on zirconium oxide is the catalyst that has the best performance in the total oxidation of methane at low temperature [1,2]. A high-activity catalyst for CO oxidation prepared with Cu supported on yttria-stabilized zirconium oxide has been reported by Dow and Huang [3]. However, the optimum Cu load is limited by the specific area of the zirconium oxide [4]. In recent years it has been shown that Cu/ZrO₂ catalysts also present high activity during methanol synthesis from CO and H₂ [5,6] and hydrogen production by steam reforming of methanol for fuel cell applications [7,8]. The zirconium oxide can also act as a catalyst by itself in reactions such as hydrogenation of CO [9] and of olefins [10]; therefore preparing zirconium oxide with a large specific area is an

interesting challenge to improve its performance as a support and its direct use as catalyst.

Different methods to prepare high-surface-area zirconium oxide have been reported in the literature. Impregnation of activated charcoal with aqueous zirconyl nitrate [11], preparation from zirconium alkoxides under hydrothermal conditions [12], substitution of zirconium by other oxides, e.g. of lanthanum, magnesium, etc. [13,14], are some examples. Sulfation of zirconium hydroxide before calcination also leads to greater stability of the material, which also has numerous catalytic applications [15]. Chuah et al. [16] have shown that the time and temperature of digestion of the hydrous zirconia obtained by precipitation of zirconium chloride with ammonium hydroxide is crucial to obtain zirconium oxides with large surface area without the need to add other oxides as dopants. The higher the digestion temperature and reflux time, the better the thermal stability of the oxide produced. Similar results have been obtained by Risch and Wolf [17], who reported an improvement in the surface area of sulfated zirconia if the freshly precipitated hydrous zirconia is refluxed at 90 °C for 20 h before the sulfation step. Later, Chuah and Jaenicke [18]

* Corresponding author. Tel.: +56 2 978 4286; fax: +56 2 699 1084.

E-mail addresses: arayap@ing.uchile.cl, arayap@cec.uchile.cl (P. Araya).

showed that using NaOH instead of ammonium hydroxide led to a zirconium oxide with a considerably larger specific area. A zirconium oxide with an extraordinarily large specific area (380 m²/g after calcining at 500 °C) has also been reported by Chuah et al. [19] by using a reflux treatment with NH₄OH of a hydrous zirconia prepared by the sol–gel method. Recently Bell and co-workers [6] study the effect of zirconia phase on the activity and selectivity of Cu/ZrO₂ catalysts during CO hydrogenation. These copper catalysts were prepared over relatively pure monoclinic or tetragonal zirconia supports with high surface areas around 150 m²/g. In all these previous works the reflux digestion treatment was done directly on the moist hydrous zirconia as an integral part of the process of synthesis.

In a previous work on CH₄ combustion over supported Pd catalysts [20], our group reported that the reflux treatment of commercial hydrous zirconia with a NaOH solution during 12 h at 100 °C, allowed remarkable stabilization of the solid structure keeping a high specific area after calcination at 700 °C. Considering the great importance that high specific area zirconia present for applications in catalysis, this work reports the results of a more detailed and thorough study on the effect of the post-synthesis treatment with NaOH and NH₄OH solutions. Special attention is given to the effect of concentration and reflux time on the physical properties of the resulting zirconium oxides. In order to verify if the post-synthesis treatment is effective in materials prepared by different methods, two hydrous zirconias obtained from different sources are studied. One of the samples studied corresponds to the same commercial material used in the previous work and the other one is a hydrous zirconia synthesized by the sol–gel method in our laboratory.

2. Experimental

The hydrous zirconias used in this work correspond to a commercial material, FZO922 from MEI Company, whose characteristics are given in Table 1, and a hydrous zirconia synthesized in our laboratory by the sol–gel method. In the latter case the hydrous zirconia was synthesized by the following method [21]. Fifty milliliters of a 70% propanol solution of zirconium isopropoxide were added slowly drop wise to a mixture of 135 ml of *n*-propanol and 4 ml of H₂O in a 500-ml round-bottom flask at 70 °C. When all the isopropoxide solution had been used, another 4 ml of water were added. The

Table 1
Characteristics reported for commercial hydrous zirconia MEI FZO922^a

Typical ZrO ₂ content range (%)	65–75
Particle size (d50) (μm)	15
Surface area (as received) (m ² /g)	480
Surface area (calcined 500 °C/2 h) (m ² /g)	100
Pore volume (as received) (cm ³ /g)	0.3
Na (%)	0.02
Cl (%)	0.02
SO ₃ (%)	<0.1
TiO ₂ (%)	0.1
SiO ₂ (%)	0.05

^a Information obtained at <http://www.zrchem.com>.

suspension was refluxed for 12 h and the solvent was then evaporated in a rotavapor. The solid obtained was dried in an oven at 105 °C overnight. These hydrous zirconias are identified as solids HZ-MEI and HZ-SG, respectively.

For the digestion treatment in basic medium, 6-g samples of the hydrous zirconia (HZ-MEI and HZ-SG) were placed in round-bottom flasks and refluxed at 100 °C for 9 h in the presence of aqueous solutions of ammonium hydroxide or NaOH. When refluxing with ammonium hydroxide, 50 ml of NH₄OH (Merck p.a., 25%, w/w) and 200 ml of distilled water were added to the solid, and the heating was done in conventional refluxing equipment without stirring the mixture. The amount of NH₄OH added was calculated to provide a NH₄OH/Zr mole ratio of about 9. After refluxing, the solid was filtrated, washed with distilled water, and dried at room temperature for 24 h. It was then placed in an oven at 105 °C overnight. The materials treated with the aqueous ammonia solution are designated as HZA-MEI and HZA-SG. When refluxing with NaOH, 6-g samples of each of the hydrous zirconias HZ-MEI and HZ-SG were added to 60 ml of a 5 M solution of NaOH (10 ml NaOH/1 g of Zr(OH)₄ ratio) and the mixture was refluxed for 9 h. The solids obtained were filtered, washed and dried in an oven at 105 °C. These materials are designated as solids HZNa-MEI and HZNa-SG.

After drying, part of the samples treated with NH₄OH (HZA-MEI and HZA-SG) or NaOH (HZNa-MEI and HZNa-SG) were calcined at 700 °C for 3 h in a muffle furnace. The calcination was carried out using a temperature ramp from room temperature to 150 °C at a rate of 1 °C/min, 2 h at 150 °C, and then to 700 °C at a rate of 5 °C/min, keeping the temperature at 700 °C for 3 h. The zirconium oxides obtained from the calcination of hydrous zirconias HZA-MEI and HZA-SG are designated as ZOA-MEI and ZOA-SG, respectively, while those obtained by calcination of hydrous zirconias HZNa-MEI and HZNa-SG are designated as ZONa-MEI and ZONa-SG, respectively. Also, a sample of the commercial hydrous zirconia (HZ-MEI) and the hydrous zirconia synthesized by the sol–gel method (HZ-SG) were calcined directly (without pretreatment) using the above program, and were used for comparison with the refluxed samples. These zirconium oxides are identified as solids ZO-MEI and ZO-SG, respectively.

The hydrous zirconias dried at 105 °C as well as the zirconium oxides obtained after calcining at 700 °C were characterized by N₂ adsorption in a Micromeritics ASAP 2010 equipment to determine their BET area and pore size distribution. All the samples were degassed at 200 °C before determining the adsorption isotherms.

The crystal structure of the zirconium oxides obtained after calcination at 700 °C was determined in a Siemens D-5000 diffractometer using Cu Kα radiation and a scan rate of 0.02°/min. The percentage of monoclinic and tetragonal structures was estimated from the area under the characteristic peaks of monoclinic phase for (1 1 $\bar{1}$) and (1 1 1) reflexes, and the tetragonal phase for the (1 1 1) reflex [16].

An OXFORD Instrument7424 EDS X-ray spectrometer attached to a LEO Electron Microscopy 1420VP SEM was used

to determine the Si content in solid zirconium oxide samples. The Si concentration in the used solutions after the reflux treatments was measured by ICP elemental analysis.

3. Results

Table 2 summarizes the physical characterization of the different solids obtained in this work as well as the material prepared in our laboratory and the commercial hydrous zirconia. All the data in Table 2 use the mass of the solid after evacuation at 200 °C (approximately 1.5 h) as reference. It is seen that both, the specific area as well as the pore volume of the commercial material determined in the laboratory, are lower than the values reported in Table 1 by MEI. These differences might be explained by a different basis used for the calculations, the specific characteristics of the batch received, or the evacuation procedure at 200 °C used in our laboratory. In any case, this work considers only the data of the commercial material reported in Table 2.

The characterization results of the hydrous zirconias, solids HZ-MEI and HZ-SG, given in Table 2, show that both materials have large specific areas, 400 and 419 m²/g, respectively. The main difference lies in the smaller pore volume (0.24 cm³/g) and mean pore diameter (24 Å) shown by the commercial with respect to that prepared by the sol–gel method, which has a pore volume of 0.35 cm³/g and a mean pore diameter of 32 Å. The adsorption isotherms and pore size distributions of these hydrous zirconias as well as of the materials obtained after refluxing are shown in Figs. 1 and 2, respectively. It is seen that both untreated materials (Fig. 1A and B) have type I isotherms, with a practically imperceptible hysteresis loop in the case of the commercial material. In the HZ-SG material the hysteresis loop is somewhat more noticeable and is located at relative pressures of 0.4 and higher, revealing the existence of a certain amount of larger diameter pores than in solid HZ-MEI. In fact, the pore size distribution curves obtained from the desorption

branch of the isotherms by the BJH method (Fig. 2A and B), show that in the commercial material there are practically no pores larger than 40 Å, while in hydrous zirconia HZ-SG there is an important amount of pores with diameters above 100 Å, reaching diameters of about 1200 Å. The cumulative pore volume curves (not included) show that in solid HZ-MEI almost 90% of the total pore volume corresponds to pores with diameters below 100 Å, while in material HZ-SG less than 60% of the pore volume is associated with pores having diameters smaller than 100 Å.

When the hydrous zirconias undergo digestion with NH₄OH, solids HZA-MEI and HZA-SG are obtained. As may be seen in Table 2, refluxing with NH₄OH causes an increase in the specific area of both materials. This enhance occurs together with an increase in pore volume and a slight increase in mean pore diameter. The adsorption isotherms of these hydrous zirconias are shown in Fig. 1C and D. It is seen that treatment with NH₄OH causes practically no changes in the shapes of the isotherms with respect to the ones they had before the treatment. Only a slight change is seen in the shape of the isotherm of solid HZA-MEI, which now shows a small hysteresis loop in the relative pressure region of 0.35–0.55, which corresponds to pores between 32 and 50 Å. The pore distribution curves of the digested hydrous zirconias, shown in Fig. 2C and D, are practically identical with those of the untreated materials. It is clear, therefore, that digestion with NH₄OH does not cause significant changes in the pore structure of the hydrous zirconia.

Contrary to what had been found previously, when the treatment is done with NaOH, there is a substantial decrease in the specific area of the hydrous zirconia. As shown in Table 2, the commercial hydrous zirconia, HZNa-MEI, has an area of 167.3 m²/g, while that prepared by the sol–gel method, HZNa-SG, decreases its area to 242.5 m²/g. Furthermore, mean pore diameter increases considerably in both hydrous zirconias digested with NaOH. The isotherms of these materials are

Table 2

Characterization of hydrous zirconia with and without pretreatment in aqueous solutions of NH₄OH and NaOH (5.0 M) and their oxides obtained after calcination

Sample description	Nomenclature ^a	S _A BET (m ² /g)	Pore volume (cm ³ /g)	Mean pore diameter (Å)	Crystalline phase XRD
Hydrous zirconia MEI					
Non-treated	HZ-MEI	400.2	0.24	24	–
Refluxed with NH ₄ OH	HZA-MEI	413.7	0.27	26	–
Refluxed with NaOH 5.0 M	HZNa-MEI	167.3	0.22	53	–
Hydrous zirconia sol–gel					
Non-treated	HZ-SG	419.2	0.35	32	–
Refluxed with NH ₄ OH	HZA-SG	447.5	0.37	33	–
Refluxed with NaOH	HZNa-SG	242.5	0.44	74	–
Zirconium oxides MEI					
Calcination of HZ-MEI	ZO-MEI	36.2	0.08	92	83% m + 17% t
Calcination of HZA-MEI	ZOA-MEI	127.7	0.12	38	t
Calcination of HZNa-MEI	ZONa-MEI	130.4	0.20	60	t
Zirconium oxides sol–gel					
Calcination of HZ-SG	ZO-SG	26.6	0.09	132	34% m + 66% t
Calcination of HZA-SG	ZOA-SG	92.2	0.14	60	t
Calcination of HZNa-SG	ZONa-SG	200.1	0.40	79	t

^a Nomenclature—HZ: hydrous zirconia; ZO: zirconium oxide; A: refluxed with ammonia solution; Na: refluxed with NaOH solution. (m): monoclinic, (t): tetragonal.

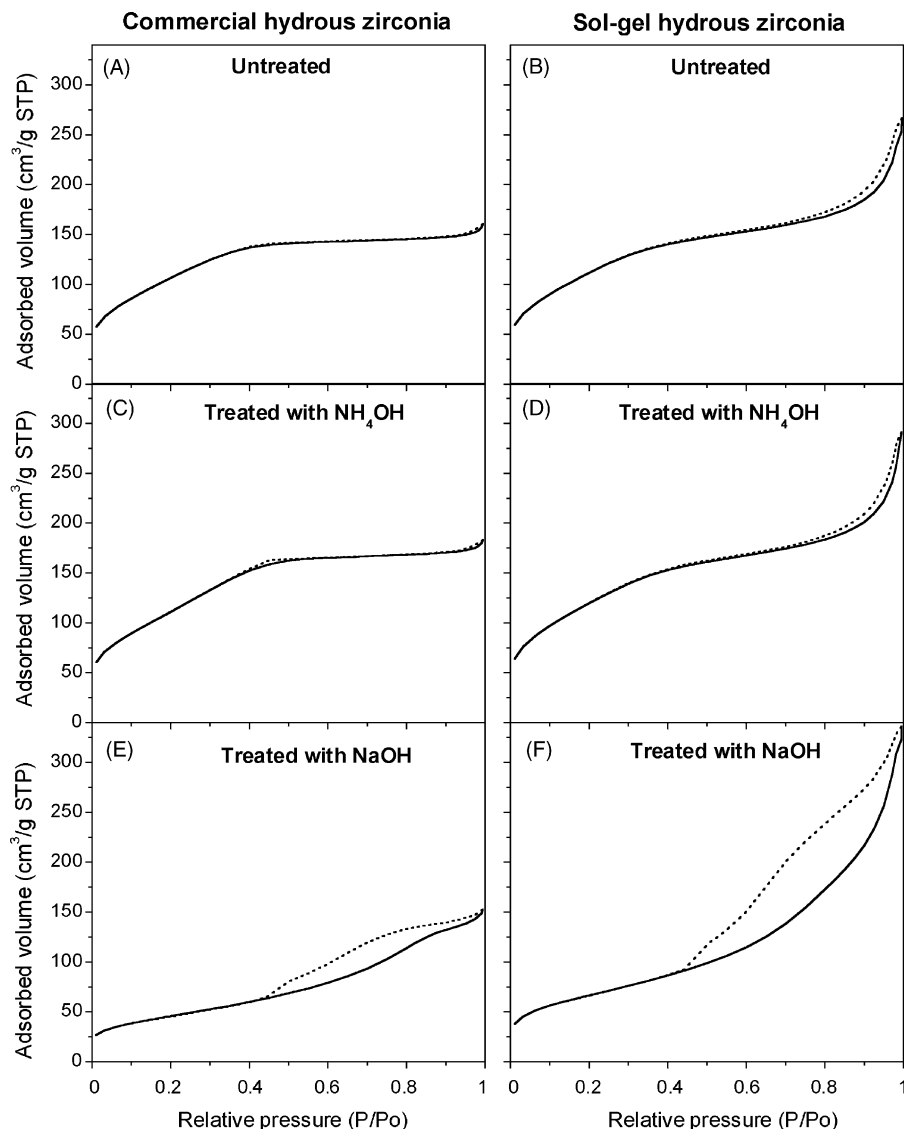


Fig. 1. N₂ adsorption (—) and desorption (---) isotherms of the original (untreated) and treated hydrous zirconias before calcination. Left column: commercial hydrous zirconia; right column: sol-gel hydrous zirconia. Untreated hydrous zirconias: (A) HZ-MEI; (B) HZ-SG. Hydrous zirconias treated with NH₄OH solution: (C) HZA-MEI; (D) HZA-S. Hydrous zirconias treated with NaOH solution: (E) HZNa-MEI; (F) HZNa-SG.

shown in Fig. 1E and F. It is seen that the isotherms of both solids show a larger hysteresis than that observed after treatment with NH₄OH, starting at relative pressures of 0.4 and extending to relative pressures close to 1. The shape of the hysteresis loops cannot be associated easily with the classical type A–E shapes [22], but the absence of pronounced steps in the adsorption or desorption branches indicates a relatively wide distribution of pore diameters. The largest difference in the shape of the isotherms is the pronounced increase in the adsorbed volume at high relative pressures shown by solid HZNa-SG, suggesting the existence of pores with large mean diameter. In fact, the pore size distributions in Fig. 2E and F show that solid HZNa-MEI has a relatively wide pore distribution, but practically no pores larger than 100 Å, while solid HZNa-SG shows a distribution with substantially larger pore diameter up to 800 Å. Therefore, in contrast with the NH₄OH treatment, digestion with NaOH produces noticeable changes in the structure of the hydrous zirconia, with a large

decrease in the BET area produced by the increase in mean pore diameter, considering that the total pore volume increases or remains constant, as can be seen in Table 2. These results suggest that the treatment with NaOH generates a re-dissolution and re-precipitation of the material that forms the hydrous zirconia. During this process a fraction of the thin walls between the pores are probably destroyed, thus increasing the average pore diameter without changing the total pore volume. As it is discussed later, the notable decrease of the specific area of hydrous zirconia after treatment with NaOH solutions is related to the high concentration of the base used (NaOH 5 M). When NaOH concentration is lower, the digestion of the hydrous zirconia is less severe, rendering hydrous zirconia very similar to the one obtained during the treatment with NH₄OH (a weak base).

The stability of these six hydrous zirconias to calcination at 700 °C for 3 h is quite different. As shown in Table 2, when the commercial hydrous zirconia and the one synthesized by the

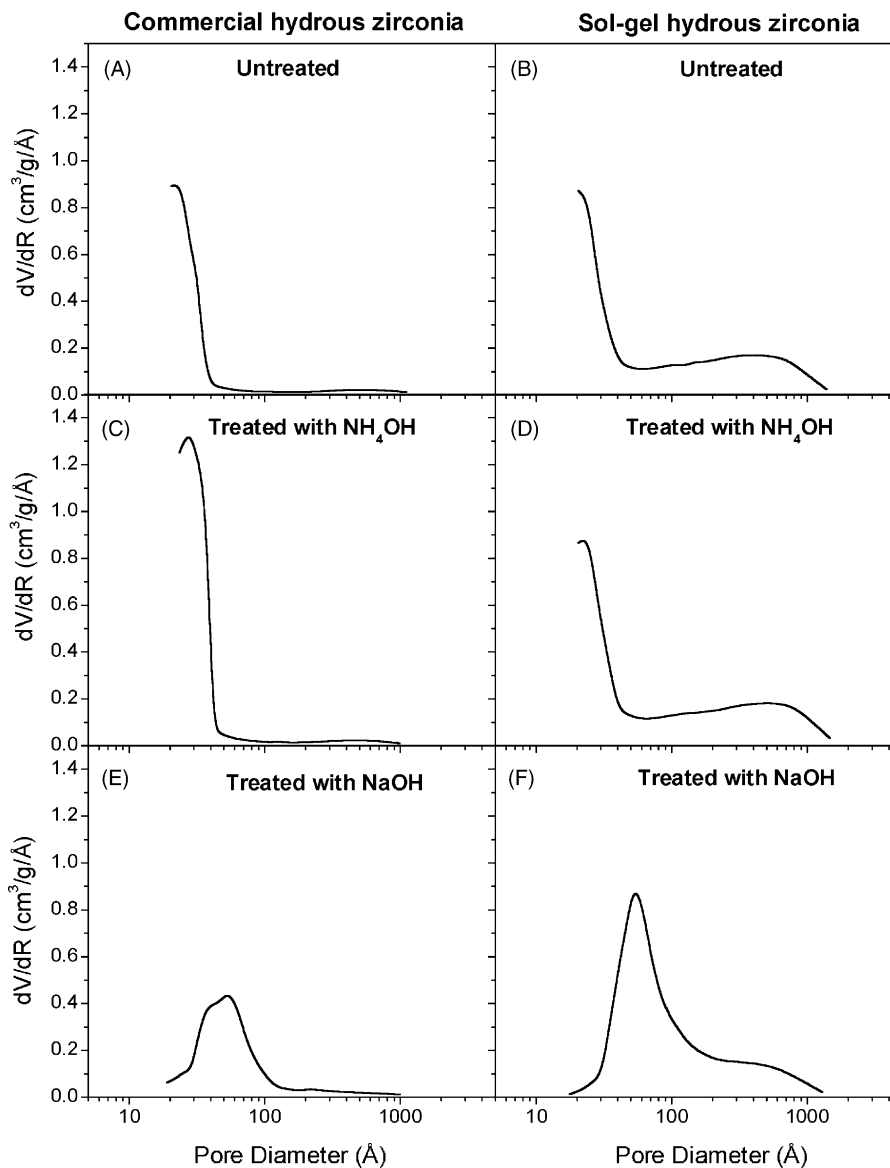


Fig. 2. Pore size distribution of the original (untreated) and treated hydrous zirconias before calcination. Left column: commercial hydrous zirconia; right column: sol-gel hydrous zirconia. Untreated hydrous zirconias: (A) HZ-MEI; (B) HZ-SG. Hydrous zirconias treated with NH_4OH solution: (C) HZA-MEI; (D) HZA-SG. Hydrous zirconias treated with NaOH solution: (E) HZNa-MEI; (F) HZNa-SG.

sol-gel method are calcined directly at $700\text{ }^\circ\text{C}$ for 3 h, the specific area of the oxides produced, ZO-MEI and ZO-SG, is 36.2 and $26.6\text{ m}^2/\text{g}$, respectively. The strong decrease of the specific area is explained by the drop in pore volume to values between 0.08 and $0.09\text{ cm}^3/\text{g}$, together with an increase in mean pore radius to $92\text{ }\text{\AA}$ in oxide ZO-MEI and to $132\text{ }\text{\AA}$ in oxide ZO-SG. The adsorption isotherms and pore size distributions of the calcined materials are shown in Figs. 3 and 4, respectively. Oxide ZO-MEI (Fig. 3A) shows a hysteresis loop similar to type A, located at relative pressures between 0.5 and 0.8 , which is characteristic of solids with a relatively narrow mesopore distribution between 50 and $110\text{ }\text{\AA}$. That is confirmed by the pore size distribution of the desorption branch (Fig. 4A). The distribution curve shows a maximum at pore diameter close to $75\text{ }\text{\AA}$. Most of the pores, about 80% of the total pore volume, have a size below $90\text{ }\text{\AA}$. In the case of the oxide ZO-SG

(Fig. 3B), the shape of the isotherm is quite different from that of the commercial oxide. There is a hysteresis loop in which the adsorption branch rises steeply to relative pressures above 0.8 that indicates the presence of large pores with diameters greater than $110\text{ }\text{\AA}$. The desorption branch also shows a large drop in the adsorbed volume as the relative pressure decreases to 0.9 , indicating the existence of pores larger than those found in the commercial material. In fact, as seen in Fig. 4B, the pore size distribution has two peaks, the smaller one below $100\text{ }\text{\AA}$, with a maximum at about $60\text{ }\text{\AA}$, while the second, larger peak, has a maximum at about $300\text{ }\text{\AA}$. In contrast with oxide ZO-MEI, in this material only 20% of the total pore volume lies below $90\text{ }\text{\AA}$. The great decrease in pore volume in both materials reflects the collapse of the structure of the hydrous zirconia during heating, indicating the low stability of the untreated materials. Moreover, as shown in Fig. 5, the crystal structure of both

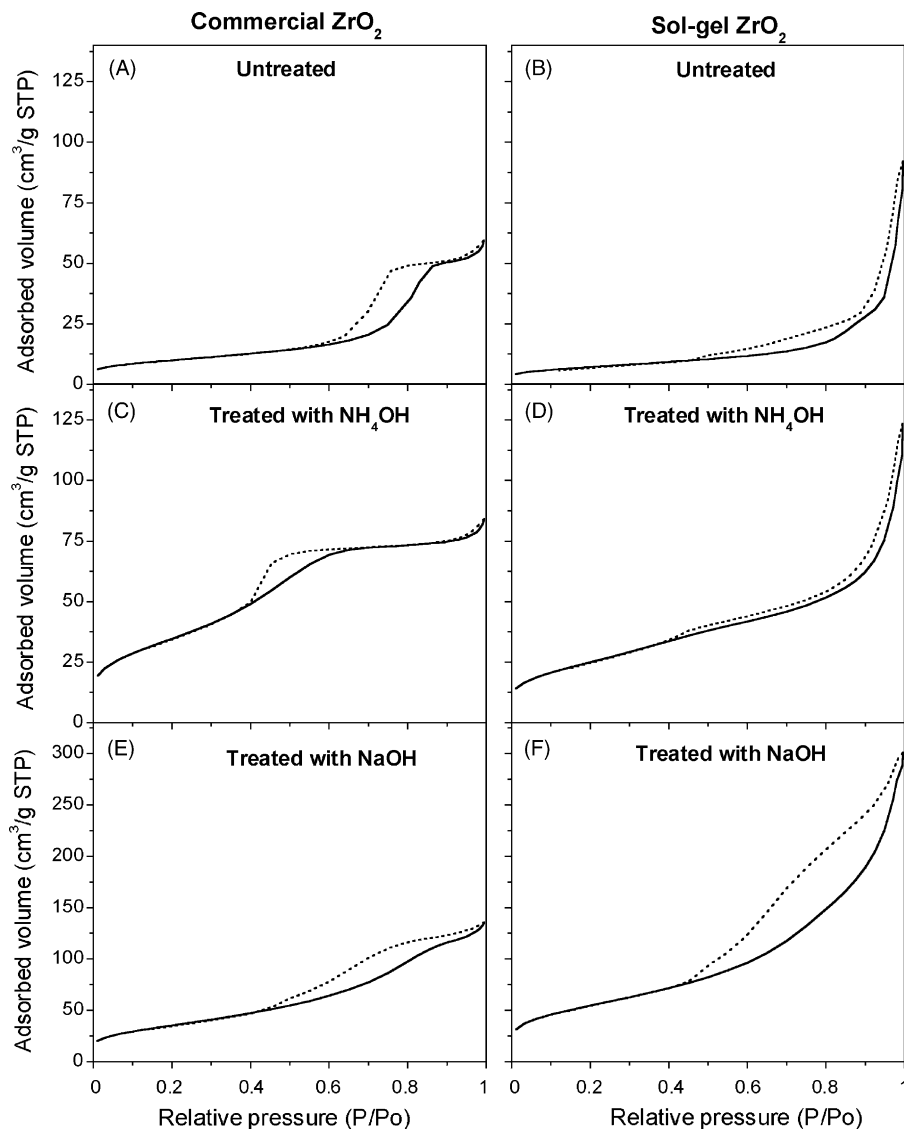


Fig. 3. N_2 adsorption (—) and desorption (---) isotherms of zirconium oxides obtained by calcination of the original (untreated) and treated hydrous zirconias. Left column: commercial hydrous zirconia; right column: sol-gel hydrous zirconia. Oxide from untreated hydrous zirconias: (A) ZO-MEI; (B) ZO-SG. Oxide from hydrous zirconias treated with NH_4OH solution: (C) ZOA-MEI; (D) ZOA-SG. Oxide from hydrous zirconias treated with $NaOH$ solution: (E) ZONa-MEI; (F) ZONa-SG.

oxides is a mixture of monoclinic and tetragonal structures, in agreement with what has been reported in the literature (see [18] and references therein).

However, when the hydrous commercial zirconia and that synthesized by the sol-gel method are previously refluxed with NH_4OH , calcination at $700\text{ }^\circ\text{C}$ produces zirconium oxides with specific areas substantially larger than those obtained by calcination of the materials without pretreatment. In fact, the oxides ZOA-MEI and ZOA-SG have specific areas of 127.7 and $92.2\text{ m}^2/\text{g}$, respectively. These areas are almost four times greater than those obtained by direct calcination of the hydrous zirconia without pretreatment, showing clearly that digestion with NH_4OH has been effective in stabilizing the structure of both hydrous zirconias. The oxides ZOA-MEI and ZOA-SG have similar pore volumes, 0.12 and $0.14\text{ cm}^3/\text{g}$, respectively, but differ in their pore size. The mean pore diameter of oxide ZOA-MEI is 38 \AA , while that of oxide ZOA-SG is 60 \AA . This shows, as expected, that the characteristics of the hydrous zirconias (HZA-

MEI and HZA-SG) affect the structure of the final zirconium oxide. In this particular case, hydrous zirconia HZA-MEI is more stable than hydrous zirconia HZA-SG with respect to the calcination process. The difference in the porous structure of the two oxides, ZOA-MEI and ZOA-SG, is shown by the shapes of the isotherms and by the pore distributions. The isotherm of oxide ZOA-MEI (Fig. 3C) has a well-defined type E hysteresis loop between relative pressures of 0.4 and 0.6 , corresponding to pores with diameters between 36 and 56 \AA . Pore size distribution in the desorption branch (Fig. 4C) is narrow, with a maximum around 35 \AA . In contrast with the previous solid, the isotherm of oxide ZOA-SG (Fig. 3D), has a slightly pronounced hysteresis loop from P/P_0 equal to 0.4 , which extends to relative pressures close to saturation, suggesting a heterogeneous distribution of pores with relatively large diameters. In fact, the pore distribution curve of this solid (Fig. 4D) shows a wide bimodal distribution, with maxima at 35 and 400 \AA . Thus, the mean pore diameter reported in Table 2 does not reflect correctly the actual mean pore diameter

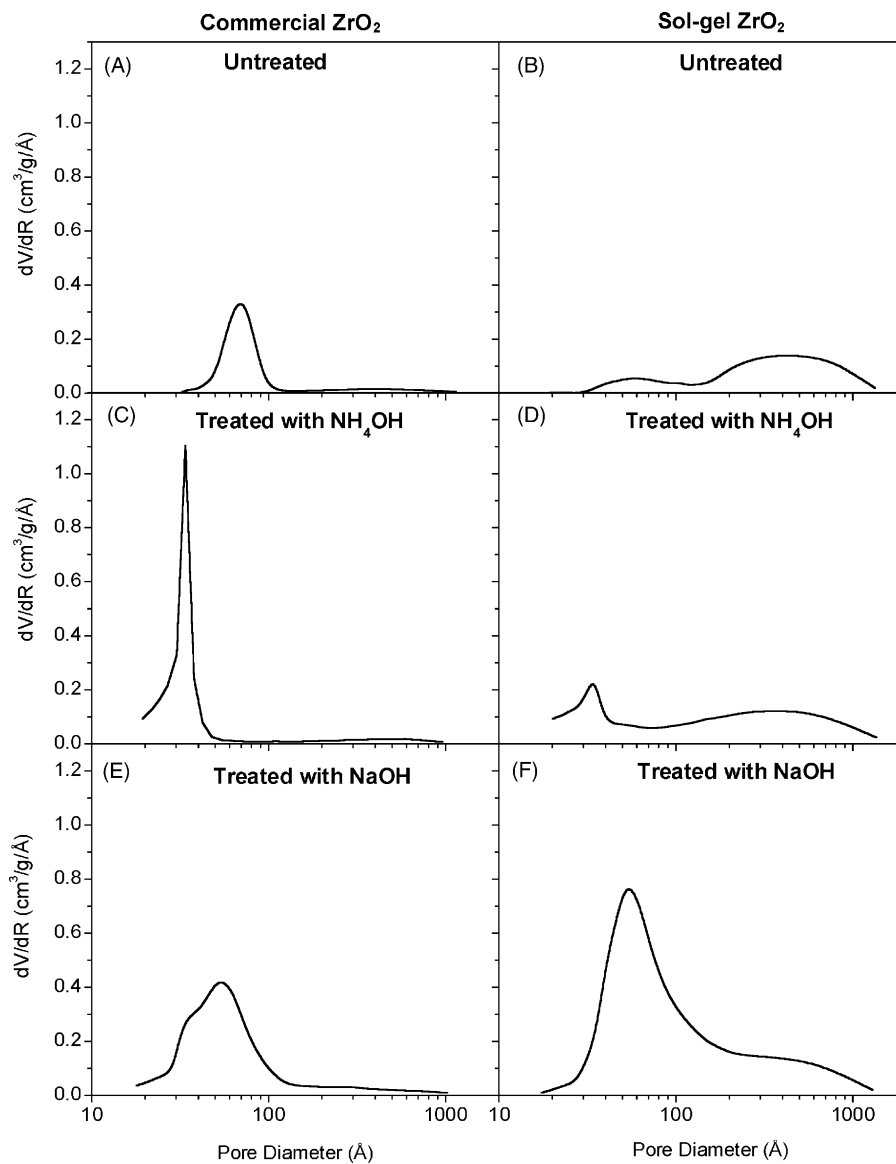


Fig. 4. Pore size distribution of zirconium oxides obtained by calcination of the original (untreated) and treated hydrous zirconias. Left column: commercial hydrous zirconia; right column: sol-gel hydrous zirconia. Oxide from untreated hydrous zirconias: (A) ZO-MEI; (B) ZO-SG. Oxide from hydrous zirconias treated with NH_4OH solution: (C) ZOA-MEI; (D) ZOA-SG. Oxide from hydrous zirconias treated with NaOH solution: (E) ZONa-MEI; (F) ZONa-SG.

of this material. When the pore size distribution of solid ZOA-SG is compared with that of the solid obtained by direct calcination of untreated hydrous zirconia, it can be concluded that the stabilizing effect of the treatment with NH_4OH is to reduce considerably the formation of large diameter pores upon calcination at high temperature. Although the porous structure of the oxides is different, it can be seen in Fig. 5 that the crystal structure of both oxides is tetragonal, indicating that the crystal structure is not affected by the pore structure of the original hydrous zirconias, but the reflux treatment stabilizes the crystal structure changing it from a mixture of monoclinic and tetragonal (Fig. 5A and B) to a pure tetragonal phase (Fig. 5C–F).

Treatment of the hydrous zirconias with NaOH also stabilizes these materials, as shown in Table 2. This result was also observed in our previous work [20]. Calcination at 700°C for 3 h of the hydrous zirconias treated with NaOH produce the zirconium oxides ZONa-MEI and ZONa-SG,

which have specific areas of 130 and $200\text{ m}^2/\text{g}$, respectively. The larger specific area of the oxide ZONa-SG is due to a greater pore volume and smaller mean pore diameter than the oxide ZONa-MEI. The smaller area of the last oxide is expected since the hydrous zirconia HZNa-MEI already possesses a smaller specific area than the HZNa-SG after the treatment with NaOH . This indicates that, contrary to what happens upon digestion with NH_4OH , the result of refluxing with NaOH is affected by the physical structure of the initial material and it produces a zirconium oxide with larger specific area when treating the hydrous zirconia HZNa-SG. Nonetheless, it must be noted that the stabilizing effect is similar for both hydrous zirconia (HZNa-SG and HZNa-MEI) provided that, upon calcination, the area of both solids decreases about 20%. The isotherms of both oxides are shown in Fig. 3E and F. It is important to point out that the isotherms are practically identical to those of the hydrous zirconias HZNa-MEI and HZNa-SG before

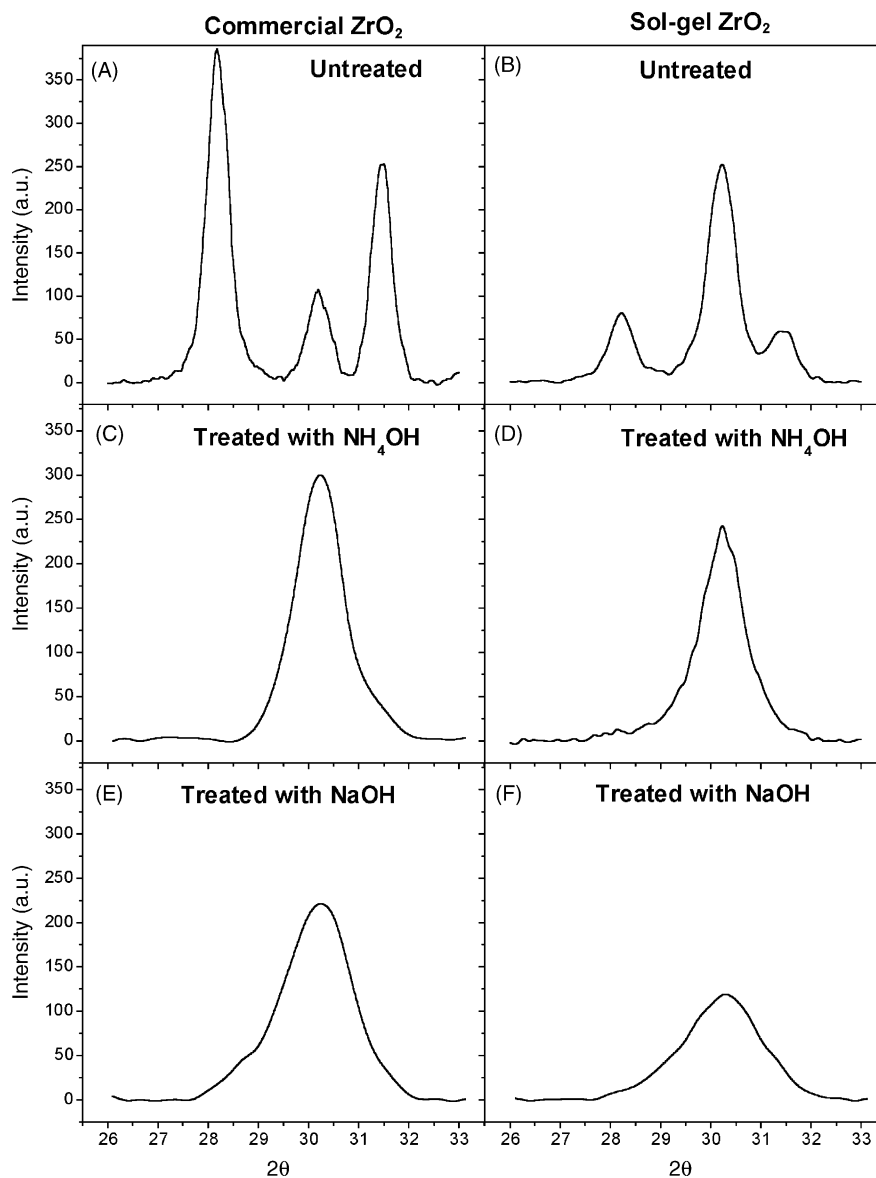


Fig. 5. XRD patterns of zirconium oxides obtained by calcination of the original (untreated) and treated hydrous zirconias. Left column: commercial hydrous zirconia; right column: sol-gel hydrous zirconia. Oxide from untreated hydrous zirconias: (A) ZO-MEI; (B) ZO-SG. Oxide from hydrous zirconias treated with NH_4OH solution: (C) ZOA-MEI; (D) ZOA-SG. Oxide from hydrous zirconias treated with NaOH solution: (E) ZONa-MEI; (F) ZONa-SG.

calcination, and therefore the pore size distributions shown in Fig. 4E and F are also very similar to those of the corresponding hydrous zirconias. This confirms the high stability achieved by the hydrous zirconias after treatment with NaOH. On the other hand, the zirconium oxides produced, ZONa-MEI and ZONa-SG, have a tetragonal crystal structure, in agreement with what was reported for materials prepared by precipitation of zirconium(IV) chloride with NaOH and digested in the mother liquor at 100 °C [18].

The influence of the concentration of the NaOH solution was studied using the commercial material. The procedure was similar as described in the experimental part, but also using 2.0 and 0.5 M NaOH solutions. The physical characteristics of these materials are given in Table 3, where the materials treated with 5.0 M NaOH solution is again included for comparison. It is seen that the higher the concentration of the NaOH solution, the lower

the specific area of the hydrous zirconia obtained. Thus, when the 0.5 M NaOH solution is used, the specific area of hydrous zirconia HZNa(0.5) is 329 m^2/g , a value considerably higher than when the NaOH 2.0 M (solid HZNa(2.0)) and 5.0 M (solid HZNa(5.0)) solutions were used, with specific areas of 228 and 167 m^2/g , respectively. Pore volume, however, does not undergo important changes with NaOH concentration remaining in the range of 0.23–0.22 cm^3/g . In contrast, the mean pore diameter increases with increasing NaOH concentration, from 28 Å for the more dilute solution to 53 Å for the treatment with 5.0 M NaOH. This increase in mean pore diameter accounts for the decrease in specific area as NaOH concentration increases. The adsorption isotherms of the hydrous zirconias and the zirconium oxides obtained after calcination at 700 °C for 3 h treated with 0.5 and 2.0 M NaOH are shown in Fig. 6. The isotherms of the hydrous zirconia and of the zirconium oxide treated with NaOH 5.0 M are

Table 3

Characterization of commercial hydrous zirconia MEI treated with aqueous NaOH solutions of different concentration and their oxides obtained after calcination

Sample description	Nomenclature	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter 4V/A BET (\AA)
Hydrous zirconia				
Refluxed with NaOH 0.5 M	HZNa(0.5)	329.4	0.23	28
Refluxed with NaOH 2.0 M	HZNa(2.0)	227.7	0.22	39
Refluxed with NaOH 5.0 M	HZNa(5.0) ^a	167.3	0.22	53
Zirconium oxides				
Calcination of HZNa(0.5)	ZONa(0.5)	173.9	0.14	31
Calcination of HZNa(2.0)	ZONa(2.0)	166.3	0.18	44
Calcination of HZNa(5.0)	ZONa(5.0) ^a	130.4	0.20	60

^a Solids HZNa(5.0) and ZONa(5.0) correspond to those identified previously as HZNa-MEI and ZONa-MEI, respectively. This new nomenclature has been used to make the NaOH concentration explicit.

also included for comparison. It is seen that the isotherm of the hydrous zirconia treated with the lowest NaOH concentration shows a small hysteresis loop between relative pressures of 0.4 and 0.6, and the shape of the isotherm is similar to that seen when

the commercial material is treated with NH_4OH . When NaOH concentration is increased to 2.0 M and above, the isotherm changes substantially, showing a wide hysteresis loop that starts at about $P/P_0 = 0.4$ and extends to pressures close to saturation.

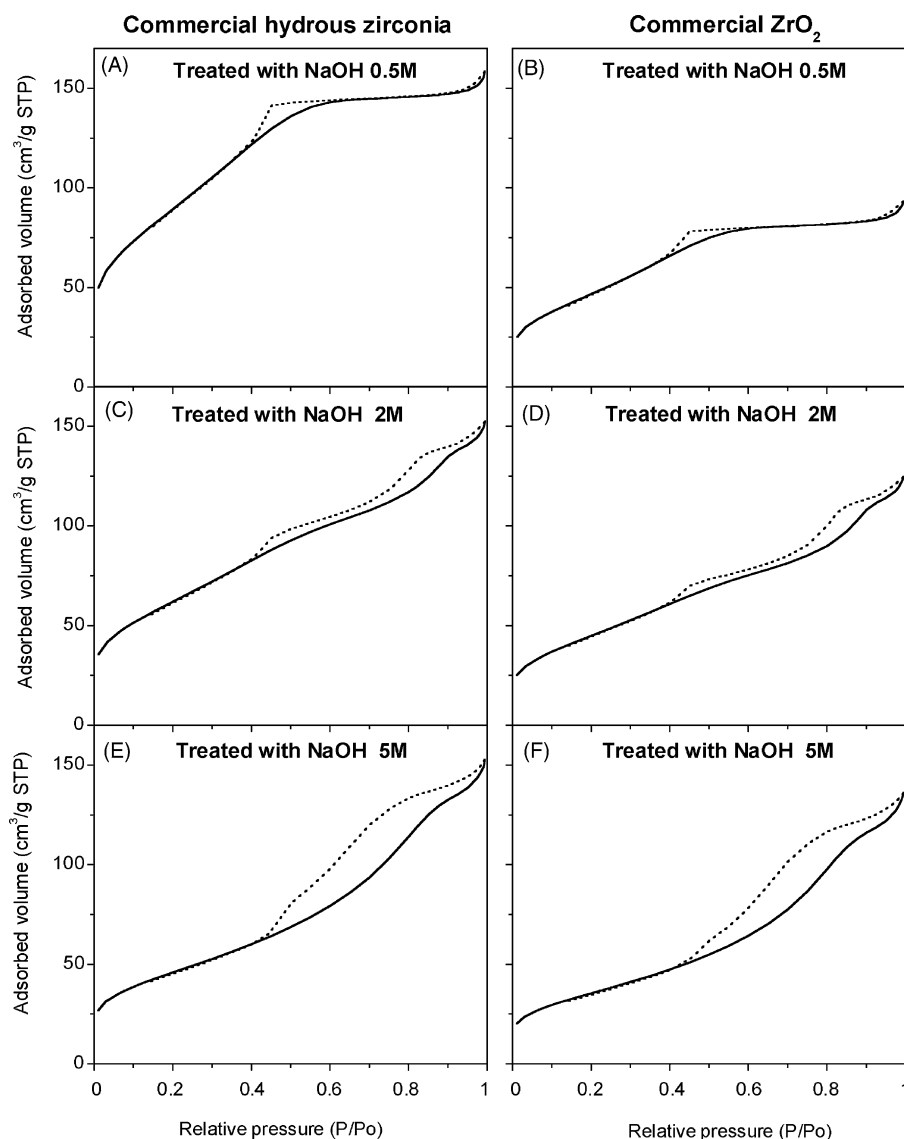


Fig. 6. N_2 adsorption (—) and desorption (---) isotherms of commercial hydrous zirconia MEI treated with 0.5, 2.0 and 5.0 M NaOH solutions and resulting zirconium oxides: (A) HZNa(0.5); (B) ZONa(0.5); (C) HZNa(2.0); (D) ZONa(2.0); (E) HZNa(5.0); (F) ZONa(5.0).

Calcination of the hydrous zirconias HZNa(0.5) and HZNa(2.0) leads to zirconium oxides ZONa(0.5) and ZONa(2.0), respectively. As seen in Table 3, zirconium oxide ZONa(0.5) has the largest specific area, 174 m²/g, decreasing to 166 m²/g for the oxide ZONa(2.0), and finally to 130 m²/g for oxide ZONa(5.0). Pore volume, on the other hand, is larger in the materials treated with a higher NaOH concentration. Even though oxide ZONa(0.5) has the largest specific area, the stability of the hydrous zirconias decreases as NaOH concentration decreases, because in this case the decrease in the specific area after calcination of the HZNa(0.5) material is 50%, while when hydrous zirconia HZNa(2.0) is calcined a 27% decrease in area occurs, and upon calcination of the HZNa(5.0) material the area decrease is only 23%. The isotherms of these oxides are shown on the right column of Fig. 6. As it can be observed, the shape of the isotherms of these oxides is practically identical to that of the hydrous zirconia, but displaced to smaller values of adsorbed gas volume. This shows, again, the high structural stability reached

with the materials treated with NaOH. In fact, the pore size distributions shown in Fig. 7 for the hydrous zirconia and the zirconium oxide confirm that, even though the pore size distributions are slightly displaced to larger pore diameters in the oxides, the isotherms and pore distributions are practically identical to those of the hydrous zirconias. What is most important is that by changing the NaOH concentration it is possible to control the mean pore size and the pore size distribution of the zirconium oxides obtained, starting from a monomodal pore distribution of small diameter at the lower NaOH concentration, going through a bimodal distribution at an intermediate NaOH concentration, to end up with an essentially monomodal distribution (with a small shoulder at smaller pore diameters) and large pore size, after treatment with the NaOH 5.0 M solution.

The effect of the reflux time was also studied using commercial hydrous zirconia. The results of the physical characterization of the materials obtained treating hydrous

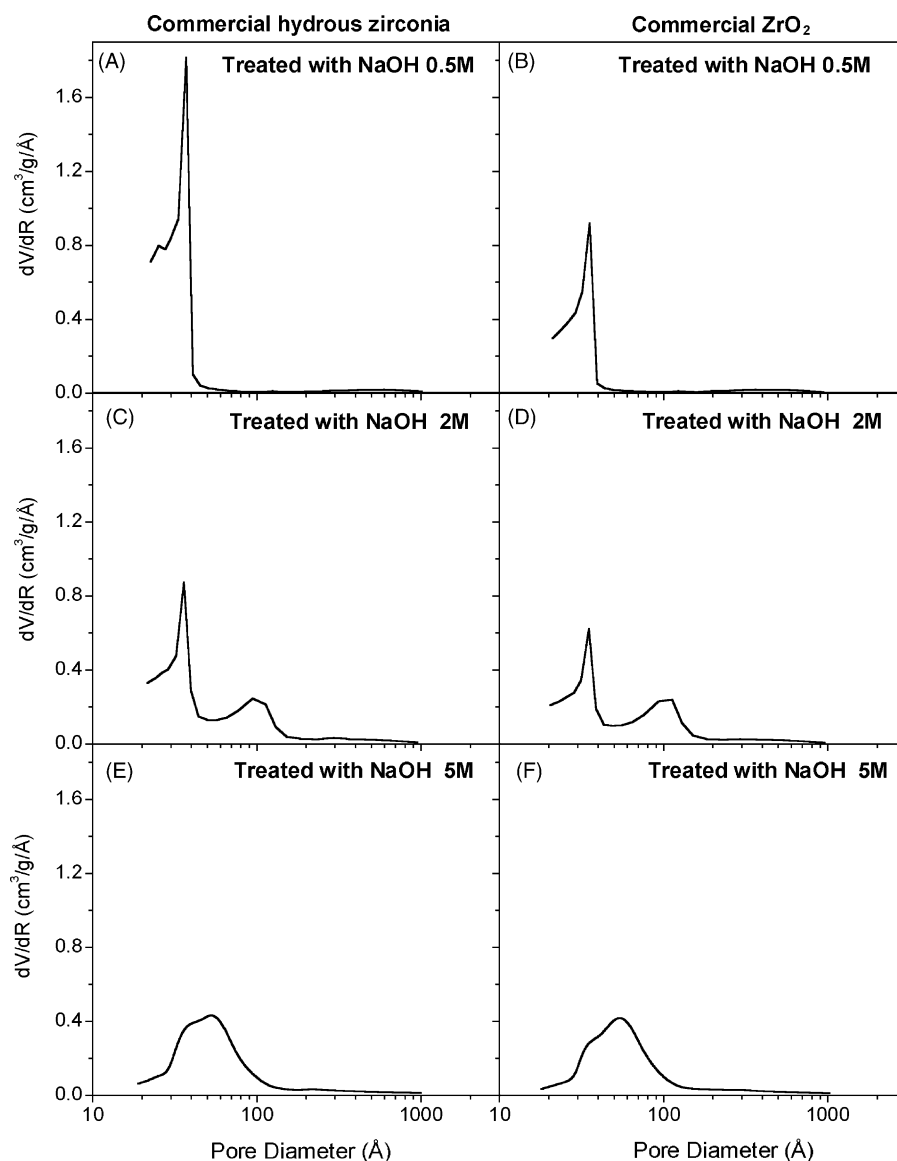


Fig. 7. Pore size distribution of commercial hydrous zirconias MEI treated with 0.5, 2.0, and 5.0 M NaOH solutions and the resulting zirconium oxides. Same nomenclature as in Fig. 5.

Table 4

Characterization of commercial hydrous zirconia MEI treated with aqueous NaOH solutions 5.0 M at different reflux times and their oxides obtained after calcination

Sample description	Nomenclature	$S_{\text{A BET}}$ (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter 4V/A BET (\AA)
Hydrous zirconia				
Refluxed during 9 h	HZNa(9) ^a	167.3	0.22	53
Refluxed during 6 h	HZNa(6)	171.4	0.23	53
Refluxed during 3 h	HZNa(3)	208.7	0.25	48
Zirconium oxides				
Calcination of HZNa(9)	ZONa(9) ^a	130.4	0.20	60
Calcination of HZNa(6)	ZONa(6)	123.4	0.20	64
Calcination of HZNa(3)	ZONa(3)	130.5	0.21	63

^a Solids HZNa(9) and ZONa(9) correspond to those identified previously as HZNa-MEI and ZONa-MEI, respectively. This new nomenclature has been used to make the time of reflux explicit.

Table 5

Characterization of commercial hydrous zirconia MEI treated with aqueous NH_4OH solutions at different reflux times and their oxides obtained after calcination

Sample description	Nomenclature	$S_{\text{A BET}}$ (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter 4V/A BET (\AA)
Hydrous zirconia				
Refluxed during 9 h	HZA(9) ^a	413.7	0.27	26
Refluxed during 6 h	HZA(6)	412.2	0.27	26
Refluxed during 3 h	HZA(3)	394.3	0.25	26
Zirconium oxides				
Calcination of HZNa(9)	ZOA(9) ^a	127.7	0.12	38
Calcination of HZNa(6)	ZOA(6)	101.7	0.12	47
Calcination of HZNa(3)	ZOA(3)	71.1	0.11	61

^a Solids HZA(9) and ZOA(9) correspond to those identified previously as HZA-MEI and ZOA-MEI, respectively. This new nomenclature has been used to make the time of reflux explicit.

zirconia during 3, 6, and 9 h with a solution of NaOH 5.0 M are showed in Table 4. As it can be observed, the shorter the time of treatment, the larger the specific areas of the hydrous zirconia. But after calcination at 700 °C for 3 h, the specific area of the different zirconium oxides obtained is practically the same, with values around 130 m^2/g . The adsorption–desorption isotherms of the hydrous zirconia and zirconium oxides treated during 3 and 6 h (not shown) are very similar to those obtained during the standard treatment of 9 h, shown in Figs. 1E and 3E, respectively. Similarly there is no important difference in the pore size distribution curves of the three final oxides. This indicates that the stabilization process of the hydrous zirconia is relatively fast, and that the treatment time can be decreased without affecting the properties of the final zirconium oxide.

In the case of the treatment with NH_4OH , however, the effect of the reflux time is very important. Table 5 shows the characterization data of the hydrous zirconia and the resulting zirconium oxides after treatment with aqueous solution of NH_4OH for different times. While the physical characteristics of the hydrous zirconia are similar regardless the treatment time, the zirconium oxides obtained after calcination at 700 °C for 3 h show that increasing the reflux time produces an important increase in their specific area. This increase of the specific area is due, essentially, to the formation of pores with smaller average size, since the pore volume is very similar in all the materials. The adsorption–desorption isotherms and the

pore size distribution of the hydrous zirconia refluxed for 3 and 6 h (not shown) are very similar to the one obtained for the material treated during 9 h (Figs. 1C and 2C, respectively). However, this is not the case for the corresponding oxides. The pore size distributions of these zirconium oxides obtained with treatment with NH_4OH during different times are shown in Fig. 8. As it can be observed, with 3 h of treatment, the material presents a bimodal distribution with pore diameters centered around 32 and 55 \AA . The increase of the treatment time produces a notorious change on the bimodal distribution, becoming a monomodal distribution with pore sizes centered near 35 \AA , after 9 h of treatment. As it was mentioned previously, the decrease in the pore diameter would explain the increase in the specific area of the zirconium oxides with the increase of the treatment time. Thus, it is clear that, contrary to what happen during a treatment with NaOH, the stabilization of the materials treated with NH_4OH is a slow process in which the reflux time is a very important variable.

4. Discussion

Various explanations for the stabilizing effect of the reflux treatment at high temperature with NH_4OH and NaOH solutions have been proposed in the literatures [16,18,19,23]. When the digestion is made in the presence of NH_4OH , Chuah et al. [16] propose that refluxing with this base at temperatures

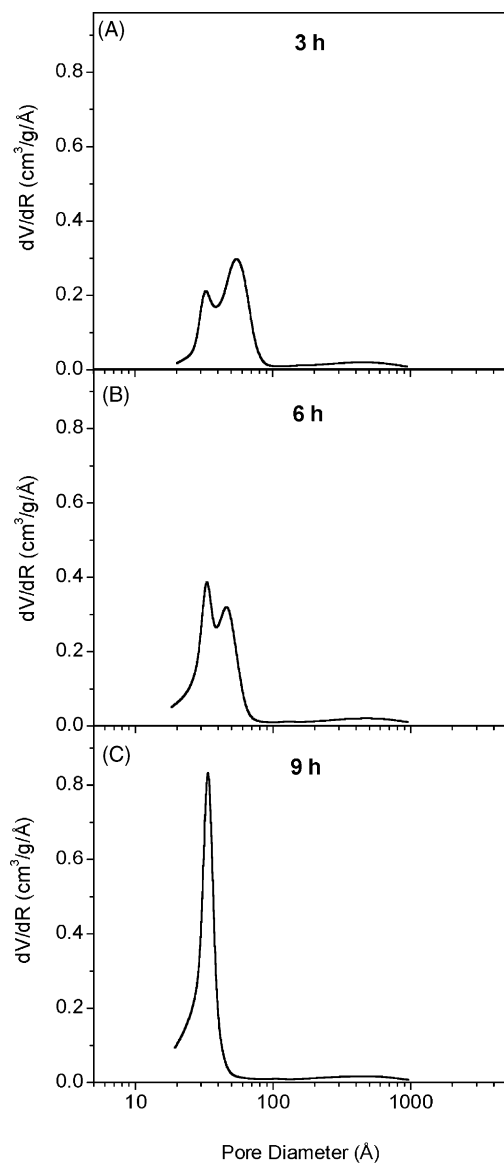


Fig. 8. Pore size distribution of zirconium oxides obtained by calcination of commercial hydrous zirconium MEI treated with aqueous NH_4OH solution at different reflux times: (A) 3 h; (B) 6 h; (C) 9 h.

higher than 80°C leads to the elimination of water from the double hydroxo groups to form oxo bridges. Later calcination of the oxo-hydroxide leads to the formation of very fine crystallites of zirconia, which results in a greater specific area of the oxide. A different explanation for the stabilization of the structure of hydrous zirconia was proposed by Chuah and Jaenicke [18,19] when digestion is done in the presence of NaOH. According to these authors, during digestion the higher temperature enhances the rate of collision between particles, increasing the rate of condensation at the junction of particles. This process leads to a thickening of the interparticle network of the hydrous oxide, retaining the porous structure during drying, when water is removed from the pores, and obtaining an oxide with larger specific area. A similar explanation was proposed later by Chuah et al. [19] for the stabilization of hydrous zirconias prepared by the sol-gel method by refluxing

with NH_4OH solutions. In a recent work, however, Yin and Xu [23] proposed that the incorporation of Si from the glass flask used for the reflux treatment may cause the stabilizing effect of the structure of hydrous zirconia prepared by a sol-gel method. They came to this conclusion based on the fact that, when using a teflon flask instead of one made of glass, the reflux of the hydrous zirconia in basic solution does not produce a stabilization of the material. They also found that the addition of a small quantity of $\text{Si}(\text{OC}_2\text{H}_5)_4$ to the solution with ZrOCl_2 , allowed the stabilization of the hydrous zirconia refluxed in teflon flasks. A similar conclusion regarding the stabilization effect of Si was reported by Sato et al. [24], when a hydrous zirconia is treated under hydrothermal conditions in a plastic flask with small pieces of quartz.

To verify if silicon was incorporated during the reflux treatments the silicon content was determined by EDS of the solid samples obtained by calcination of the hydrous zirconia refluxed for 9 h with NH_4OH (solid ZOA) and NaOH 5.0 M (solid ZONa), corresponding to the most extreme treatments conditions (the longest reflux time for NH_4OH treatment and maximum NaOH concentration). EDS analysis shows that for the zirconium oxide prepared by NaOH reflux (ZONa) the average Si content is 5.2%, very similar to the value reported by Yin and Xu for the material refluxed with NaOH in glass flask [23], whereas no Si was detected in the solid treated with NH_4OH (ZOA). Clearly, the difference in the silicon content must be related with the amount of silica that can be dissolved from the flask walls during the treatments with NH_4OH and NaOH solutions. Therefore, two experiments were performed in order to reproduce the reflux treatment, but without placing hydrous zirconia in the ball. The objective was to determine the silicon content in these solutions. In the case of reflux treatment with NH_4OH solution for 9 h, elemental analysis by ICP indicated a Si concentration of 0.17 g/l, while in the solution obtained from reflux with NaOH 5.0 M for 3 h, a significantly higher Si concentration was detected, ca. 5.9 g/l. It is clear then that the amount of silicon dissolved from the walls of a glass ball during the treatment in NH_4OH is considerable less than the one obtained in presence of concentrated NaOH, even when the reflux time with NaOH is only 3 h. These results explain the high silicon content in the sample treated with NaOH 5.0 M, while in the sample refluxed with NH_4OH , the Si concentration was below detection limits.

The previous results suggest that the stabilization of the samples treated with NH_4OH , for reflux times under 9 h cannot be related with incorporation of silicon in the solid, but rather to a dehydration mechanism as the one proposed by Chuah et al. [16]. This would explain why, when the zirconium oxide is stabilized by a NH_4OH treatment, there is a strong influence of the refluxing time on the final surface area of the solid. On the other hand, in the case of the samples treated with NaOH, the presence of Si indicates that the stabilization of the material is probably related to its incorporation into the structure of the hydrous zirconia, as previously suggested in the literature [23,24]. To separate the effects of the digestion in NaOH solution and the silicon incorporation on the physical characteristics of the solids, additional experiments were

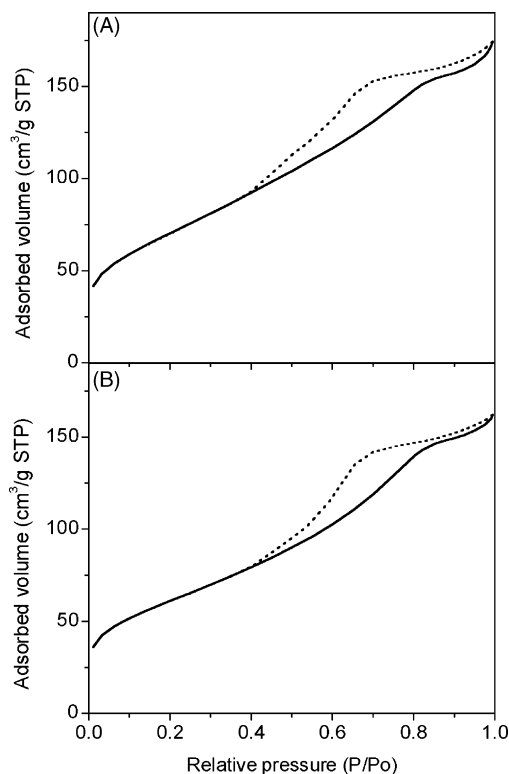


Fig. 9. N_2 adsorption (—) and desorption (···) isotherms of hydrous zirconia treated with NaOH 5.0 M solution for 3 h: (A) reflux in glass flask; (B) reflux in plastic flask.

carried out using plastic flasks (PP Plastibrand) to avoid unwanted contamination with Si. Fig. 9A and B shows the isotherms of the samples obtained after treating hydrous zirconia MEI with a NaOH solution 5.0 M for 3 h, using a glass flask (Fig. 9A) and a plastic flask (Fig. 9B). As it can be observed, the adsorption–desorption isotherms are practically identical in both cases, as well as the specific areas (around $300 \text{ m}^2/\text{g}$ in both cases). However, the area of the oxide obtained after calcining the sample treated in the plastic flask was only $30 \text{ m}^2/\text{g}$. This value is very similar to the area of the oxide obtained from the hydrous zirconia MEI without any reflux treatment ($36 \text{ m}^2/\text{g}$). Thus, it is clear that the NaOH treatment determines the porous structure of the refluxed hydrous zirconia, but, in absence of silicon, the zirconium oxide is not stabilized by a treatment with concentrated NaOH solutions.

It was also found that the stabilization of the hydrous zirconia is a very fast process in the presence of an external Si source. Indeed, when the hydrous zirconia MEI is refluxed in the plastic flask for 30 min with a solution 5.0 M of NaOH, and 5 g/l of silicon are added (as sodium silicate), the resulting zirconium oxide maintains a specific area $147 \text{ m}^2/\text{g}$, a value almost five times higher than the one obtained in absence of silicon, even for this short time reflux. This short time needed to stabilize the hydrous zirconia is consistent with the results reported by Sato et al. [24], who proposed that silicon deposited on the surface of the primary particles of hydrous zirconia, avoiding further aggregation upon calcination. The almost null

dependence of the specific area of the zirconium oxides with the refluxing times in NaOH solution (Table 4) can be then explained by a high concentration of silicon in solution, that quickly stabilizes the structure of hydrous zirconia independently of the treatment time.

Regarding the effectiveness of the post-synthesis treatments for the structure stabilization of the hydrous zirconias, it is important to mention that in the case of treatment with NH_4OH , stabilization of the commercial hydrous zirconia by a short post-synthesis reflux (9 h) is comparable to that achieved by Chuah et al. [16] by precipitation of zirconium(IV) chloride with NH_4OH followed by digestion in the mother liquor for 48 h at 100°C . Thus, even though in our case the hydrous zirconias were obtained by a completely different method, this treatment with NH_4OH leads to a material with a thermal stability similar to that found by those authors. In the case of treatment with NaOH solutions a comparison cannot be made since Chuah and Jaenicke [18] do not report on the silicon incorporation in the final oxides.

It is therefore clear that by applying these short post-synthesis treatments it is possible to stabilize the materials obtained by completely different methods to a similar extent as those achieved if the digestion is included as an integral part of the synthesis. The presence of Si is however needed when the treatment is made with NaOH solutions. The effectiveness of these treatments depends on the characteristics of the original hydrous zirconias. Regardless the source of silicon, either from the dissolution of the glass walls or by addition of a Si containing compound, an adequate choice of the post-synthesis treatment, particularly the NaOH concentration would allow to control the physical characteristics of the resulting zirconium oxides.

5. Conclusions

The post-synthesis treatment of different hydrous zirconias either with NaOH or with NH_4OH has been shown to be effective in the stabilization of their structure, leading to an increase in the specific area of the zirconium oxide obtained after calcination of the hydrous zirconias at 700°C for 3 h. It was found that the stabilization of the hydrous zirconia by reflux in NaOH solution is related to the addition of Si into their structure. The physical properties, pore size distribution and pore volume, are controlled by the treatment conditions as reflux time and alkali concentration. The final structure is stabilized by the silicon added to the solution either from an external source or from dissolution of the flask glass walls. On the contrary, for the treatment with NH_4OH solutions for reflux times under 9 h, there was no evidence of Si addition.

The results of this work show that with a relatively simple treatment it is possible to substantially improve the thermal stability of hydrous zirconias synthesized by routes that originally lead to materials having low thermal stability. In treatments with NaOH solution, the alkali concentration allows to control the pore size distribution of the zirconium oxides. In the case of treatments with a NH_4OH solution, the porous structure can be the controlled by modifying the reflux time.

These results are of particular interest in catalytic reactions where the selectivity or product distribution can be selectively controlled through the average pore size.

Acknowledgements

This work was financed by FONDAP project 11980002. Donation of hydrous zirconia by Magnesium Elektron Inc. MEI (USA) is gratefully acknowledged.

References

- [1] P. Gelin, M. Primet, *Appl. Catal. B* 39 (2002) 1.
- [2] M. Zwinkels, S. Jaras, P. Menon, *Catal. Rev.-Sci. Eng.* 35 (3) (1993) 319.
- [3] W. Dow, T. Huang, *J. Catal.* 160 (1996) 171.
- [4] T. Huang, K. Lee, H. Yang, W. Dow, *Appl. Catal. A* 174 (1998) 199.
- [5] M.D. Rhodes, A.T. Bell, *J. Catal.* 233 (2005) 198.
- [6] M.D. Rhodes, K.A. Pokrovski, A.T. Bell, *J. Catal.* 233 (2005) 210.
- [7] H. Purnama, F. Girgsdies, T. Ressler, J.H. Schattka, R.A. Caruso, R. Schomäcker, R. Schlögl, *Catal. Lett.* 94 (2004) 61.
- [8] A. Szizybalski, F. Girgsdies, A. Rabis, Y. Wang, M. Niederberger, T. Ressler, *J. Catal.* 233 (2005) 297.
- [9] W. Johnson, J. Eckerdt, *J. Catal.* 126 (1990) 146.
- [10] K. Domen, J. Kondo, K. Maruya, T. Onishi, *Catal. Lett.* 12 (1992) 127.
- [11] M. Osawa, M. Kimura, *J. Mater. Sci. Lett.* 9 (1990) 446.
- [12] M. Inoue, H. Kominami, T. Inui, *Appl. Catal. A* 97 (1993) L25.
- [13] B. Fegley, P. White, H. Bowen, *Am. Ceram. Soc. Bull.* 64 (1985) 1115.
- [14] P. Mercera, J. Van Ommen, E. Doesburg, A. Burggraaf, J. Ross, *Appl. Catal.* 71 (1991) 363.
- [15] G. Yadav, J. Nair, *Micropor. Mesopor. Mater.* 33 (1999) 1.
- [16] G. Chuah, S. Jaenicke, S. Cheong, K. Chan, *Appl. Catal. A* 145 (1996) 267.
- [17] M. Risch, E. Wolf, *Appl. Catal. A* 172 (1998) L1.
- [18] G. Chuah, S. Jaenicke, *Appl. Catal. A* 163 (1997) 261.
- [19] G. Chuah, S. Liu, S. Jaenicke, J. Li, *Micropor. Mesopor. Mater.* 38 (2000) 381.
- [20] S. Guerrero, P. Araya, E.E. Wolf, *Appl. Catal. A* 298 (2006) 243–253.
- [21] T. Lopez, UNAM, Mexico, personal communication.
- [22] J. Thomas, W. Thomas, *Principles and Practice of Heterogeneous Catalysis*, VCH, Weinheim (Federal Republic of Germany), 1997, pp. 276–282.
- [23] S.-F. Yin, B.-Q. Xu, *Chemphyschem* (3) (2003) 277.
- [24] S. Sato, R. Takahashi, T. Sodesawa, S. Tanaka, K. Ogura, J. Catal. 196 (2000) 190.